

Japanese Patent Laid-Open No.: 236945/1996

Laid-Open Date : September 13, 1996

Application No. : 328298/1995

Application Date : November 22, 1995

Convention Priority :

Convention Date : December 2, 1994

Appln. No. : 329645/1994

Country : JP

Request for Examination : Not made

Inventor(s) : Yoshiichi Yamagami, et al

Applicant(s) : Nippon Paint K.K.

[Title of the Invention]

Production process for a multi-layered substrate

[Abstract] (Amended)

[Subject]

Production of a multi-layered substrate having an insulative layer excellent in bondability of a conductor pattern, capable of insuring electric insulation for a long time and excellent in resolution upon development.

[Means for Solution]

A process for producing a multi-layered substrate which comprises [1] laminating a light sensitive composition formed into a film-shape on an insulative material previously formed with a conductor pattern, exposing and then dissolving a

not-light irradiated area, heat curing a not-dissolved region, applying electroless copper plating thereon and, further forming a copper plating layer, and applying exposure, development and etching by way of a photomask to form a conductor pattern, in which the film-like light sensitive composition contains at least 50% by weight of a bisphenol epichlorhidrin type resin containing photosensitive functional groups and heat setting functional groups.

[Scope of the Claim for Patent]

[Claim 1] A process for producing a multi-layered substrate which comprises repetitively applying the steps [1] to [6] including [1] a step of laminating a light sensitive composition formed into a film shape on an insulative material previously formed with a conductor pattern, [2] a step of exposing the laminated film-like light sensitive composition by way of a negative type photomask, [3] a step of dissolving a region not irradiated with light by the exposure, [4] a step of heat curing a region not dissolved by the step [3], [5] a step of applying electroless copper plating on the film-like light sensitive composition heat cured by the step [4] and, further, forming a copper plating layer further thereon with or without electrolysis copper plating, and [6] a step of forming a light sensitive etching resist layer to the surface of the copper plating layer formed by the step [5] and then applying exposure, development and etching by way of a photomask to which a circuit pattern is drawn, wherein the film-like light sensitive composition contains at least 50% by weight of a bisphenol epichlorohydrin type phenol resin containing light sensitive functional groups and heat curable functional groups.

[Claim 2] A production process for a multi-layered substrate as defined in claim 1, wherein the film-like light sensitive composition contains an inorganic filler.

substrate as defined in claim 3, wherein the bisphenol epichlorohydrin type resin contains 0.5 to 4/kg of (meth)acryloyl groups as the light sensitive functional groups and contains 0.5 to 2 mol/kg of carboxyl groups as the thermosetting functional groups.

[Claim 5] A production process for a multi-layered substrate as defined in claim 1, wherein the bisphenol epichlorohydrin type resin has a weight average molecular weight of 8,000 to 40,000 and contains chalcone as the light sensitive functional groups.

[Claim 6] A production process for a multi-layered substrate as defined in claim 5, wherein the bisphenol epichlorohydrin type resin contains 0.1 to 1 mol/kg of chalcone as the light sensitive functional group and contains 0.5 to 1.5 mol/kg of epoxy group as the heat setting functional group.

[Claim 7] A production process for a multi-layered substrate as defined in claim 5 or 6, wherein the film-like light sensitive composition contains 10 to 30% by weight of an organic solvent.

[Claim 8] A process for producing a multi-layered substrate which comprises repetitively applying the steps [1] to [6] including [1] a step of laminating a light sensitive composition formed into a film shape on an insulative material previously formed with a conductor pattern, [2] a step of exposing the laminated film-like light sensitive composition by way of a negative type photomask, [3] a step of dissolving a region not irradiated with light by the exposure, [4] a step of heat curing a region not dissolved by the step [3], [5] a step of applying electroless copper plating on the film-like light sensitive composition heat cured by the step [4] and, further, forming a copper plating layer further thereon with or without electrolysis copper plating, and [6] a step of forming a light sensitive etching resist layer to the surface of the copper plating layer formed by the step [5] and then applying exposure, development and etching by way of a photomask to which a circuit pattern is drawn, wherein the film-like light sensitive composition contains at least 50% by weight of a bisphenol epichlorohydrin type resin-containing chalcone as the light sensitive functional group and epoxy group as heat curing functional group, as well as 10 to 30% by weight of an organic solvent and the process comprises evaporating the organic solvent at a temperature lower than the heat-curing temperature of the film-like light sensitive composition after the step [2] described above and, subsequently, practicing the

step [3].

[Description of the Invention]

[0001]

[Technical Field of the Invention]

This invention concerns a production process for a multi-layered substrate of producing, by a build-up method, a printed wiring substrate for electronics, that is, a multi-layered substrate requiring high density wirings in a substrate as small as possible.

[0002]

[Prior Art]

Along with advance of electronic technology, it has been intended to increase the density and increase the operation speed in electronic equipments such as computers. For printed wiring substrates used for them, multi-layered substrates in which wiring circuits are stacked in plural layers are used with an aim of increasing the density for attaining the foregoing object.

[0003]

In a multi-layered substrate for use in electronic equipments, extremely high electric insulation is required between conductor layers, since when electric insulation between the conductor layers is lowered during use of electronic equipments, erroneous signal operation occurs leading to

erroneous operation and the equipment does not operate correctly. In recent years, as the weight, thickness and the size of the wiring substrates become reduced, the electric insulation for the insulative layer has become more important factor not only at the initial stage but also during continuous use. Further, in view of the durability of the insulation , it is required that the insulation layer and the conductor layer are bonded strongly.

[0004]

In the multi-layered substrates described above, conductor layers separated by an insulative layer are connected with each other by way of metal plated in through holes or conductors filled in via holes. However, since the through holes or the via holes are apertured by using a drill, there is a considerable limit for reducing the diameter of the holes. Further, for connecting conductor layers separated by the insulative layer from each other even between the two layers, it is necessary to form through holes for the entire circuit, which increases the number of holes, making it difficult to increase the wiring density.

[0005]

In order to overcome such drawback, it has been tried to produce a multi-layered substrate by a build-up method. As the technique for producing the multi-layered substrate by the build-up method, Japanese Patent Publication No. 55555/1992,

for example, discloses a technique of producing a multi-layered substrate by repeating coating a liquid mixture formed by dispersing at least one particulate material selected from heat resistant fine resin powder and inorganic fine particles which are soluble to an acid or oxidizer and previously put to curing treatment in a light sensitive resin less soluble to the acid or oxidizer on an insulative material formed with a conductor pattern by a roller coating method, certain coating method or screen printing method, drying and then exposing the same by way of a photomask, dissolving a not-exposed portion to conduct aperturing and, subsequently, applying electroless plating to the insulation layer. Japanese Patent Laid-Open No. 143492/1990 discloses a technique in connection with the technique described above of conducting aperturing under the irradiation of a laser beam.

[0006]

[Subject to be Solved by the Invention]

However, in the techniques described above, since bubbles tended to be formed when the liquid insulative material was coated and dried as the wiring density of the printed substrate become higher, aging deterioration in electric insulation was caused due to bubbles present in the insulative layer. Further, when the thickness of the insulation layer was increased in order to ensure the electric insulation, it rather tended to cause bubbles and, as a result, led to contradiction that the



aging insulation property is lowered.

[0007]

In the production process for the multi-layered substrate by the build-up method, Japanese Patent Laid-Open No. 136575/1993 discloses a method of laminating an insulative film of a predetermined composition in stead of the liquid resin composition, as a technique of using an insulative film with no bubbles. However, in this technique, since the insulative film comprises an epoxy resin, a phenol resin, a thermoplastic resin and an cationic photo-polymerization initiator as essential ingredients, and the epoxy resin of a small molecular weight is photocured by the cationic photo-polymerization initiator, and the phenol resin and the thermoplastic resin as other essential ingredients have no light sensitive groups in the resin, insurance of electric insulation for a long period of time is insufficient. Further, in this technique, only the epoxy resin concerns curing reaction by the irradiation of light and other resins comprising about 30 to 85% by weight of the composition do not concern the photocuring reaction, so that resolution of the pattern upon development was extremely poor. Further, since the cationic polymerizate of the epoxy resin is chain extended by of ether bonds, the insulative film not always has good adhesion with the conductor pattern formed by copper plating and reliability for duration was poor.

[0008]

As a method of insuring adhesion between the insulative layer and the conductor layer, a method of applying a roughening treatment to the insulative layer and the conductor layer thereby forming unevenness to enhance the bondability between them has been known. As such a method, Japanese Patent Publication No. 55555/1992 discloses a technique of dissolving particles incorporated in a light sensitive resin thereby forming concave portions by the roughening treatment. However, the composition in this method requires a property not soluble to an organic solvent in an ink but soluble to a roughening liquid and thus this is an extremely limited composition. Further, a chemical such as strong acid or strong alkali has to be used as the roughing liquid.

[0009]

A method of improving the conformability of the insulative layer to an underlying layer in stack, thereby insuring the adhesion, Japanese Patent Laid-Open No. 67881/1993 proposes a method of coating a liquid insulative material on the surface of a substrate formed with a conductor pattern, followed by drying and then laminating a film-like insulative material. However, this method requires to previously coat and dry a liquid insulative material upon stacking the insulation layer, which complicates the step and deteriorates the productivity.

[0010]

In view of present situations, this invention intends to provide a process for producing a multi-layered substrate having an insulative layer free from bubbles that deteriorates the insulation property, excellent in adhesion with the conductor pattern with no particular roughening treatment, excellent in adhesion with the conductor pattern, capable of insuring electrical insulation for a long period of time and excellent in resolution upon development.

[0011]

[Means for Solution of Subject]

The feature of this invention resides in a process for producing a multi-layered substrate which comprises repetitively applying the steps [1] to [6] including [1] a step of laminating a light sensitive composition formed into a film shape on an insulative material previously formed with a conductor pattern, [2] a step of exposing the laminated film-like light sensitive composition by way of a negative type photomask, [3] a step of dissolving a region not irradiated with light by the exposure, [4] a step of heat curing a region not dissolved by the step [3], [5] a step of applying electroless copper plating on the film-like light sensitive composition heat cured by the step [4] and, further, forming a copper plating layer further thereon with or without electrolysis copper plating, and [6] a step of forming a light sensitive etching resist layer to the surface of the copper plating layer formed

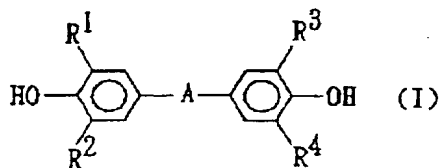
by the step [5] and then applying exposure, development and etching by way of a photomask to which a circuit patten is drawn, wherein the film-like light sensitive composition contains at least 50% by weight of a bisphenol epichlorhidrin type phenol resin containing light sensitive functional groups and heat curable functional groups. This invention is to be described in details.

[0012]

In this invention, the insulation layer is laminated with a film-like light sensitive composition containing bisphenol epichlorohydrin as a light sensitive resin. The bisphenol epichlorohydrin type resin in this specification is not restricted to a narrow meaning but means a resin having a unit obtained by ring-opening addition reaction of a bisphenol compound represented by the general formula (I).

[0013]

[formura-1]



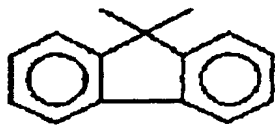
[0014]

(where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$ , which may be identical or different with each other, each represents a hydrogen atom, an alkyl group of 1 to 4 cabin atoms or a halogen atom, A represents  $-\text{O}-$ ,  $-\text{CH}_2-$ ,

-C(CH<sub>3</sub>)<sub>2</sub>-, -CO-, -C(CF<sub>3</sub>)<sub>2</sub>-, -Si(CH<sub>3</sub>)<sub>2</sub>- or represents:

[0015]

[formura-2]



[0016]

or means direct coupling between a phenyl group and a phenyl group. In the film-like light sensitive composition described above, the content of the bisphenol epichlorohydrin type resin is at least 50% by weight. When the content is less than 50% by weight, photo via holes can not be formed in a fine shape and conduction reliability between upper and lower circuits by copper plating is insufficient, so that the content is defined within the range described above.

[0017]

The bisphenol epichlorohydrin type resin may be any of resins of large molecular weight and having light sensitivity and heat reactivity. For example those containing (meth)acryloyl group as the light sensitive functional group and containing carboxyl group as the heat curable functional group can be used. The concentration in the (meth)acryloyl phenol in the bisphenol epichlorohydrin type resin is 0.5 to 4 mol/kg. When the concentration of the (meth)acryloyl group contained is less than 0.5 mol/kg, difference in the solubility

to the liquid developer by the photo-irradiation is insufficient to worsen the contrast. On the other hand, when it exceeds 4 mol/kg, cross linking density by the curing reaction is excessively high to reduce the inter-crosslinking molecular weight to form a hard and brittle film, which causes crackings due to the change of the amount of heat generation between the current supply state and the not current supply state to worsen the durability. It is preferably from 0.6 to 3 mol/kg and, more preferably, 0.8 to 2 mol/kg.

[0018]

The concentration of the carboxyl group in the (meth)acryloyl group-containing bisphenol epichlorohydrin type resin is 0.5 to 2 mol/kg. When the concentration of the carboxyl group is less than 0.5 mol/kg, the cross linking density is excessively low to deteriorate the insulation reliability and the plating resistance. On the other hand, when it exceeds 2 mol/kg, the cross-linking density increases excessively to worsen the durability and the adhesion with the copper plating of the multi-layered substrate. It is preferably from 0.7 to 1.5 mol/kg.

[0019]

The weight average molecular weight of the (meth)acryloyl group-containing bisphenol epichlorohydrin type resin is 3,000 to 20,000. When the weight average molecular weight is less than 3,000, the shape of the formed film is difficult to be

retained. On the other hand, when it exceeds 20,000, a not irradiated portion is not dissolved to the liquid developer to worsen the contrast. It is preferably from 4,000 to 15,000, more preferably, 5,000 to 10,000.

[0020]

The content of the (meth)acryloyl group-containing bisphenol epichlorohydrin type resin is preferably from 50 to 85% by weight as the solid content. When the content is less than 50% by weight, photo via holes can not be formed in a fine shape and conduction reliability between the upper and lower circuits formed by copper plating is poor. When it exceeds 85% by weight, flexibility is poor.

[0021]

In this invention, when the (meth)acryloyl group-containing bisphenol epichlorohydrin type resin is used, a curing reaction agent is incorporated in order to provide a heat curing reactivity. There is no particular restriction on the curing reacting agent and it can include, for example, phenol novolac type epoxy resin, cresol novolac epoxy resin, biphenyl type epoxy resin, and epoxy resin or epoxide compounds having one or more epoxy groups such as triglycidyl isocyanurate, and hydroxy alkylamide. The addition amount of the curing reaction agent is preferably from 5 to 20% by weight. When the addition amount is less than 5% by weight, the heat resistance and the insulation property are poor. On the other hand, when

bisphenol epichlorohydrin type resin, a light sensitive monomer and a photo-polymerizing initiator are further added to the light sensitive composition. The light sensitive monomer has a function of controlling the contrast, improving the light sensitivity, controlling the cross-linking density and controlling the flexibility upon film formation. The light sensitive monomer has no particular restriction so long as it is a compound having one or more (meth)acryloyl groups and can include, for example, mono(meth)acrylates such as methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate and (meth)acrylate; di(meth)acrylates such as ethylene glycoldi(meth)acrylate and neopentyl glycol di(meth)acrylate; and polyfunctional (meth)acrylates such as trimethylol propane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate and acryl oligomer. The addition amount of the light sensitive monomer is preferably from 5 to 35% by weight. When the addition amount is less than 5% by weight, it results in insufficient contrast, sensitivity failure or lack of flexibility. On the other hand, when it exceeds 35% by weight, it forms a tacky film making it difficult to retain the shape and form a hard or brittle film.



[0023]

The photo-polymerization initiator has no particular restriction and can include known initiators, for example, benzoin such as benzoin, benzoin methylether and benzoin propyl ether; acetophenones such as acetophenone, dimethoxyphenylacetophenone and dichloroacetophenone; anthraquinones such as methyl anthraquinone and amylnanthraquinone; and thioxanthenes. They can be used in combination with known photo-polymerization promoters such as benzoic acid type or tertiary amine type promoters. The addition amount of the photo-polymerization initiator is preferably from 1 to 10 % by weight. When the addition amount is less than 1% by weight, it has no effect and when it exceeds 10% by weight, it is economically disadvantageous.

[0024]

In a case of using the (meth)acryloyl group-containing bisphenol epichlorohydrin type resin, since most of light sensitive monomers are liquid, there is no particular requirement of using an organic solvent for maintaining the film property but it may be used as desired.

[0025]

In this invention, an inorganic filler is added to the film-like light sensitive composition. The inorganic filler has a function of improving the heat resistance, adhesion, flexibility and peeling strength of copper plating. There is

no particular restriction on the inorganic filler and it can include, for example, barium sulfate, silica, zircon, calcium carbonate, alumina and talc.

[0026]

The addition amount of the inorganic filler is preferably 3 to 30% by weight. When the addition amount is less than 3% by weight, the heat resistance and the peeling strength of the copper plating is insufficient. On the other hand, when it exceeds 30% by weight, although the heat resistance is improved, since particulate inorganic material is dispersed in the light sensitive composition, the light sensitivity is lowered and the photo via holes are not formed in a fine cylindrical form. Further, since the resin component is decreased, the peeling strength of the copper plating is lowered, or since the film becomes extremely rigid, crackings tend to be formed.

[0027]

In this invention, for improving the heat resistance, adhesion and flexibility, an organic gel may be used in combination with the inorganic filler. The organic gel can include acrylic gel particles or vinylic gel particles formed by copolymerizing polyfunctional cross linking monomers to conduct polymerizing reaction in organic resin particle synthesis reaction such as emulsion polymerization, suspension polymerization and dispersion polymerization, and then drying or applying solvent substitution with an appropriate organic

solvent.

[0028]

In this invention, a surface controlling agent may also be added further to the film-like light sensitive composition. The surface controlling agent has a function of avoiding involvement of bubbles and leveling failure upon coating and drying the light sensitive composition to form into a film shape. The surface controlling agent has no particular restriction and can include, for example, fluoro type, silicon type or acrylic type defoamers or leveling agents. The addition amount of the surface controlling agent is preferably 0.05 to 2% by weight in the solid content of the film-like light sensitive composition. When the addition amount is less than 0.05% by weight, no aimed effect can be obtained. On the other hand, when it exceeds 2% by weight, it forms pin holes or skims.

[0029]

In this invention, a multi-layered substrate can be produced by stacking a plurality of circuit layers by repeating the steps [1] to [6], including [1] a step of laminating a light sensitive composition formed into a film shape on an insulative material previously formed with a conductor pattern, [2] a step of exposing the laminated film-like light sensitive composition by way of a negative type photomask, [3] a step of dissolving a region not irradiated with light by the exposure, [4] a step of heat curing a region not dissolved by the step

previously formed with the conductor pattern. There is no particular restriction on the insulative material and, for example, those used generally such as a glass epoxy plate can be used preferably.

[0031]

The light sensitive composition formed into the film-like shape can be obtained by drying and coating the light sensitive composition on a base material. There is no particular restriction on the base material and, for example, a polyester film such as of polyethylene terephthalate can be used suitably in view of the strength and the releasability. The coating can be conducted by coating the light sensitive composition described above adjusted to a proper viscosity by an organic solvent on the base material. The light sensitive composition

can be prepared by mixing a blend by a customary method. The coating may be conducted by a customary method using, for example, a roller coater, spray coater, knife coater, die coater or lip coater. The drying can be conducted by evaporating the organic solvent to substantially 0 or to a predetermined amount by a hot blow drying furnace, infrared drying furnace or the like. After the drying, it is taken up in a slightly tacky state while being passed through film thickness controlling rolls. In this process, another releasing film or releasing cover is preferably applied over the dried film. As the releasing film, a polyethylene film can be used suitably. The thickness of the light sensitive composition formed into the film-like shape, while different depending on the thickness of the conductor pattern, is usually preferably from 40 to 100  $\mu\text{m}$  thickness as dry thickness. When it is less than 40  $\mu\text{m}$ , the insulation reliability is poor. On the other hand, when it exceeds 100  $\mu\text{m}$ , the thickness of the multi-layered substrate is excessively increased.

[0032]

In the step [1] above, the light sensitive composition formed into the film-like shape is laminated on the insulative material. The lamination can be conducted by a customary device such as a vacuum laminator. In this case, for completely laminating the film to the gaps of the conductor pattern, it is preferred to use a heating device in combination thereby

[2] described above, a step of drying the laminated film-like light sensitive composition may be added as required.

[0035]

In the step [2] described above, the laminated film-like light sensitive composition is exposed by way of a negative type photomask. The exposure can be conducted with a sufficient quantity of light to photo-polymerizing reaction of the light

sensitive composition by using, for example, high pressure mercury lamps or metal halide lamps. For the negative type photomask, those used customarily can be used. For example, those formed by coating a light sensitive emulsion on a polyester film, on which an original silver salt photographic film is projected, and then developed and cured can be used suitably.

[0036]

In the step [3] described above, the region not photo irradiated by the exposure is dissolved to conduct development. The liquid developer used for the development has no particular restriction so long as it does not dissolve the exposed portion but dissolve the not-exposed portion thereby forming a photo via holes. Those that evaporate at a heat curing temperature of the light sensitive composition and do not remain in the insulative layer after drying are preferred. In a case of using the (meth)acryloyl group-containing bisphenol epichlorohydrin type resin, the liquid developer usable in the step [3] described above can include, for example, weakly alkaline solutions such as of sodium metasilicate.

[0037]

In the step [4] described above, the region not dissolved by the step [3] above is heat cured. The heat curing can be conducted by using, for example, a hot blow circulation type drying furnace, an infrared drying furnace or a far infrared

surface of the heat cured insulative layer. In this process, a physical method such as buffing, sanding or jet scrubbing is preferred for the polishing, and an oxidizer such as permanganic acid or chromic acid can be used suitably for the chemical etching.

[0039]

In the step [6] described above, a conductor pattern is formed on the surface of the copper plating layer formed by the step [5] described above. The conductor can be formed by a customary method and, for example, it can be applied by forming an etching resist, then forming a copper pattern by acid etching and, subsequently, peeling the etching resist. In this process, a light sensitive etching resist is preferably used and the conductor pattern is formed after forming the resist layer by applying exposure, development and etching by way of a photomask that is drawn with a circuit pattern and, subsequently, the



light sensitive etching resist is peeled. In this invention, a multi-layered substrate having desired number of circuit layers can be produced by repeating the steps [1] to [6] described above.

[0040]

In other embodiment of this invention, as the bisphenol epichlorohydrin type epoxy resin described above, a bisphenol epichlorohydrin type epoxy resin containing chalcone as the light sensitive functional group and containing epoxy group as the heat curing functional group is preferred. The chalcone has a property that identical kind of polyfunctional groups are reacted and photo-polymerized to each other by photoradical reaction. The concentration of chalcone contained in the bisphenol epichlorohydrin type epoxy resin is from 0.1 to 1 mol/kg. When the concentration of the chalcone contained is less than 0.1 mol/kg, the photo-crosslinking reaction does not proceed and no contrast is obtained. On the other hand, when the concentration exceeds 1 mol/kg, it results in difficulty in the intermolecular cross linking and, further, it is excessively rigid when formed into the film-like shape to lack in the flexibility, and worsen the durability of the multi-layered substrate. It is preferably from 0.2 to 0.8 mol/kg and, more preferably, 0.3 to 0.7 mol/kg.

[0041]

In the chalcone-containing bisphenol epichlorohydrin

type epoxy resin, acrylic monomer or acrylic oligomer which is customary means in the light sensitive resin composition has a large difference in the reaction speed and can not be used in the blend.

[0042]

The concentration of the epoxy group in the chalcone-containing bisphenol epichlorohydrin type epoxy resin is from 0.5 to 1.5 mol/kg. When the concentration of the epoxy group is less than 0.5 mol/kg, the cross linking density is excessively lowered to deteriorate the insulation reliability and plating resistance. On the other hand, when it exceeds 1.5 mol/kg, the cross linking density increases excessively to worsen the durability and adhesion with the copper plating of the multi-layered substrate. It is preferably from 0.6 to 1.2 mol/kg and, more preferably, 0.7 to 1.0 mol/kg.

[0043]

The weight average molecular weight of the chalcone-containing bisphenol epichlorohydrin type epoxy resin is 8,000 to 40,000. When the weight average molecular weight is less than 8,000, the light-irradiated portion is reacted and polymerized to become insoluble to the liquid developer while the not-irradiated portion is left in the soluble state as it is to worsen the contrast of the images when they are formed. When the weight average molecular weight exceeds 40,000, the

not-irradiated portion is not dissolved to the liquid developer to worsen the contrast. It is preferably from 10,000 to 30,000 and, more preferably, 12,000 to 20,000.

[0044]

The content of the chalcone-containing bisphenol epichlorohydrin type epoxy resin is preferably 50 to 80% by weight in the film-like light sensitive composition. When the content is less than 50% by weight, photo via holes can not be formed in a fine shape and the conduction reliability between upper and lower circuits formed by copper plating is insufficient. On the other hand, when it exceeds 80% by weight, the content of the inorganic filler and the organic solvent are decreased to cause lack of flexibility. It is more preferably from 55 to 75% by weight.

[0045]

In this invention, in a case of using the chalcone-containing bisphenol epichlorohydrin type resin, an organic solvent may be added to the film-like light sensitive composition. The organic solvent moderates rigidity of the film formed by the light sensitive composition, provides an appropriate flexibility to avoid a disadvantage of causing cracks in the film. Further, when the film is laminated to the base material having the conductor pattern, the solvent improves intrusion of the film into the pattern to enhance the adhesion with the base material. There is no particular

restriction on the organic solvent so long as it dissolves the bisphenol epichlorohydrin type resin. Those having such a volatility as not easily volatilizing from the film but volatilizing during heat curing reaction and not remaining at all in the film not to lower the insulation property are preferred and, those having a boiling point of about 160 to 270°C are preferred. Such organic solvent can include, for example, diethylene glycol monoethyl ether, diethylene glycol dimethyl ether, diethylene glycol butyl ether, butyrolactone, triethylglycol dimethyl ether, propylene glycol methyl ether acetate and propylene glycol propyl ether.

[0046]

The addition amount of the organic solvent is preferably 10 to 30 % by weight. When the addition amount is less than 10% by weight, softening property and adhesion upon lamination can not be insured. On the other hand, when it exceeds 30% by weight, it is difficult to maintain the film shape, the tensile strength upon lamination is low and the film is cut in the course of the process to cause defects.

[0047]

In the film-like sensitive composition, a heat curing agent that takes place addition reaction with the epoxy group, a heat curing catalyst and a surface controlling agent may also be added. The heat curing agent that takes place the addition reaction with the epoxy group is preferably a latent curing

agent with which proceeds reaction only upon heating at a relatively high temperature. Curing agent, cross linking agent and the like of high reaction rate usually employed for the curing reaction with the epoxy group are not suitable in the invention using the film of the epoxy resin since the epoxy resin is in a 2-component type, and they are not preferred also in view of the storage stability.

[0048]

The latent curing agent can include those known agents, for example, dicyan diamide, Lewis acid complexes, imidazole compounds, organic acid hydrazides, diamino maleonitrile, melamine and derivatives thereof, polyamine salts and microencapsulated curing agents. The addition amount of the heat curable agent that takes place addition reaction with the epoxy group is determined depending on the amount and the reaction equivalent of the epoxy resin and, generally, it is preferably from 2 to 8% by weight. When the addition amount is less than 2% by weight, the heat curing reaction does not exceeds effectively to deteriorate the heat resistance and the insulation property. When it exceeds 8% by weight, since the curing agent to the epoxy group is generally a polar compound, the residues are increased to lower the insulation property.

[0049]

The latent curing agent may be used in combination with the heat curing catalyst and the heat curing catalyst has no

containing bisphenol epichlorohydrin type epoxy resin, a step of evaporating the organic solvent in the laminated film-like light sensitive composition to dry the same may be added optionally after the step [2] and before the step [3] in order to control the developing speed or the shape of the photo via holes. In this case, the drying conditions preferably include such temperature and time that the organic solvent in the film-like light sensitive composition is evaporated and temperature at which the film-like light sensitive composition is heat cured. The temperature and the time are different depending on the kind of the film-like light sensitive composition and the organic solvent contained therein and it is generally about 60 to 100°C for 15 to 60 min. As the temperature is lower, drying time is longer. As the temperature is higher, the drying time is shorter, but heat curing reaction tends to occur to cause heat fogging. In the drying, the base material of the light sensitive composition has to be peeled.

[0051]

In the case of using the chalcone-containing bisphenol epichlorohydrin type epoxy resin, the liquid developer usable in the step [3] can include, for example, ether alcohols such as methyl ether, ethyl ether, ethyl ether acetate of ethylene glycol; methyl ether, dimethyl ether, ethyl ether, diethyl ether, butyl ether, dibutyl ether of diethylene glycol; methyl ether, dimethyl ether of diethylene glycol; methyl ether, dimethyl ether, ethylether, ethyl ether acetate of propylene glycol: lactones such as  $\alpha$ -butyrolactone and  $\epsilon$ -caprolactone: amides such as dimethyl formamide and dimethyl acetoamide. Two or more of them may be used in combination.

[0052]

In this invention, since the light sensitive composition having the composition containing the high molecular weight bisphenol epichlorohydrin type resin and the organic filler is used, excellent adhesion under lapse of time with the conductor pattern can be maintained and an insulation layer of excellent electrical insulation property can be laminated with no particular roughening treatment. Further, since the light sensitive composition having the composition described above can be formed into a film-shape of excellent moldability, releasability, transferability and storability, an insulation layer with no bubbles can be laminated and, further, it can satisfy the light sensitivity and the chemical resistance, particularly, electroless copper plating resistance which are

[Example 1]

To 90 parts by weight of a mixed solvent varnish comprising the triethylene glycol dimethylether (A) and propylene glycol methylether acetate (B) of bisphenol epichlorohydrin type epoxy resin having a weight average molecular weight of 15,000, chalcone concentration of about 0.54 mol/kg and about 0.8 mol/kg of epoxy concentration (solid content 55 wt%, A/B = 18/27), were mixed 10 parts by weight of propylene glycol methylether, 4 parts by weight of R-972 (super fine particulate silica, manufactured by Nippon Aerosil Co., Ltd.), 6 parts by weight of fine seal T-32 (fine particulate silica, manufactured by Tokuyama Co.) and 0.1 parts by weight of BYK-070 (silicon defoamer, manufactured by Bic Chemi Co.), and they were dispersed by ceramic-coated three rolls to a grain size of 10  $\mu\text{m}$  or less. On the other hand, 1 part by weight of dicyan diamide dissolved in 4 parts by weight of dimethyl acetoamide was mixed therewith and, further, 5 parts by weight



of propylene glycol methyl ether was added. The liquid mixture was coated on a polyester film of 25  $\mu\text{m}$  by using a lip reverse coater to a thickness of about 130  $\mu\text{m}$  and then dried for about 2 min in a tunnel furnace controlled to 60-100°C. The dried product had 79% by weight of solid contents. While hot, a polyethylene film of 30  $\mu\text{m}$  thickness was laminated on the film-like product, passed through rolls with an adjusted gap and then taken up on a 3 inch plastic pipe. Thus, a film of a light sensitive composition of about 80  $\mu\text{m}$  thickness was obtained.

[0055]

An insulative material made of glass epoxy previously formed with a conductor pattern was heated by being passed through external heated rolls set to 150°C, while a film of the light sensitive composition obtained as described above and previously peeled with the cover film of the polyethylene was laminated on both surfaces of the insulative material by a vacuum laminator while being in contact with rolls set at 50°C. After cooling the laminated substrate, a negative photomask for aperturing photo via holes was placed on the base film of the polyester and exposed at a light intensity of 3,000 mJ/cm<sup>2</sup> on a light sensitive composition by an exposure machine using metal halide lamps. After peeling the polyester base film from the light sensitive composition, the substrate was left in a drying furnace set to 90°C for 30 min, and then a not-exposed

portion was dissolved with  $\gamma$  butyl lactone. After washing with water, it was left for 20 min in a drying furnace at 80°C to remove water content. When the substrate was heat cured for 90 min in a drying furnace at 140°C, a cup-shaped photo via hole was finely opened with the upper diameter of about 150  $\mu\text{m}$  and the lower diameter of about 100  $\mu\text{m}$ .

[0056]

After buffing the surface of the heat cured light sensitive composition by about 7  $\mu\text{m}$  to condition the surface, solvent swelling and chemical etching were conducted by an ordinary desmearing treatment and electroless plating was applied to from a copper foil to about 0.3  $\mu\text{m}$  thickness. Electric copper plating was applied thereon to obtain a copper plating layer of about 20  $\mu\text{m}$  in total. After forming a light sensitive etching resist (Photo ED system P-1000, manufactured by Nippon Paint Co., Ltd.) on the copper plating, exposure was applied, using a copper circuit forming pattern mask, followed by development, etching and resist peeling to form a second layer conductor pattern on the light sensitive composition. After the step of laminating the light sensitive composition, the same steps were repeated to obtain a third layer conductor pattern. Subsequently, solder resist was applied thereon to manufacture a multi-layered substrate having six layers in total. Conduction between each of the circuits was complete.

[0057]

In the step of copper plating after conditioning the surface of the light sensitive composition described above, a test plate with the copper plating thickness of 35  $\mu\text{m}$  in total was prepared and notched such that the width of the copper plating wheel was 10  $\mu\text{m}$ . When it was peeled at 90° by a tensile tester for measuring the adhesion strength between the copper plating wheel and the light sensitive composition, it was 1200 g/cm. After the step of forming an IPC comb pattern by etching the copper plating foil formed on the light sensitive composition and laminating the light sensitive composition thereon, an IPC comb pattern quite identical with that of the under layer was formed also to the upper layer so as to overlap the lower layer, without opening photo via holes by way of the light sensitive composition by the same method. After applying a solder resist on the most upper layer pattern, it was set in a pressure cooker test machine controlled at 121°C, 2 atm. and 85% RH under an application of DC voltage of 30 V to the upper and lower comb patterns respectively and an insulation reliability test was conducted. The resistance value between the upper and lower layers was initially  $8 \times 10^{13} \Omega$  and the resistance value after 300 hr was  $3 \times 10^8 \Omega$ . This was an insulation reliability causing no problem at all in view of practical use.

[0058]

[Example 2]

A film of a light sensitive composition of about 75  $\mu\text{m}$  thickness with the solid content of 84% by weight was obtained by drying the film-shape light sensitive composition for 150 sec in a tunnel furnace upon preparation of the composition in Example 1. A six-layered substrate was obtained by repeating same method as in Example 1 except for using the film and setting the temperature of the heating roll for heating the film of the light sensitive composition peeled with the polyethylene cover film to 100°C. The results of the test for the peeling strength and the insulation reliability for the thus obtained copper plating foil and the light sensitive composition of the obtained multi-layered substrate were identical with those in Example 1.

[0059]

[Example 3]

A 6-layered substrate was obtained in the same manner as in Example 1 except for changing the steps in the stage of exposing, drying and developing the substrate laminated with the film of the light sensitive composition for forming photo via holes in Example 1, such that the polyester base film was peeled and drying at 90°C for 30 min before exposure and bringing the negative photomask in direct contact with the light sensitive composition for exposure and developing with  $\gamma$  butylolactone just after exposure. The results for the peeling strength and the insulation reliability test for the copper

plating foil and the light sensitive composition of the resultant multi-layered substrate were identical with those in Example 1.

[0060]

[Example 4]

100 parts by weight of a propylene glycol propylether varnish of bisphenol epichlorohydrin type epoxy resin having a weight average molecular weight of 6,000, an acryloyl concentration of about 2.5 mol/kg and a carboxyl group concentration of about 1.2 mol/kg (solid content 75%), 25 parts by weight of propylene glycol methylether, 36 parts by weight of barium sulfate, 5.5 parts by weight of R-972 (super fine particulate silica, manufactured by Nippon Aerosil Co., Ltd.), 40 parts by weight of dipentaerythritol hexaacrylate, 15 parts by weight of triglycidyl isocyanurate, 10 parts by weight of bis(N,N-dihydroxyethyl) adipamide, 2 parts by weight of Illugacure-907 (photopolymerization initiator, manufactured by Chiba Geigy Co., Ltd.) and 0.5 parts by weight of BYK-070 (silicone defoamer, manufactured by Bic Chemi Co.) were blended and dispersed by a ceramic coated sand grind mill to a grain size of 10  $\mu\text{m}$  or less. The liquid dispersion was coated to a thickness of about 110  $\mu\text{m}$  on a polyester film of 25  $\mu\text{m}$  thickness by using a die coater and dried for about 1 min in a tunnel furnace controlled to 50-100°C. The organic solvent could scarcely be detected in the dried products. While slightly hot,

previously peeled with the cover film of the polyethylene was laminated on both surfaces of the insulative material by a vacuum laminator while being in contact with rolls set at 70°C. After cooling the laminated substrate, a negative photomask for aperturing photo via holes was placed on the base film of the polyester and exposed at a light intensity of 600 mJ/cm<sup>2</sup> on a light sensitive composition by an exposure machine using super high mercury lamps. After peeling the polyester base film from the light sensitive composition, the substrate was the not-exposed portion was dissolved with an 1% aqueous solution of sodium carbonate. After washing with water, it was dried for 10 min in a drying furnace at 80°C to remove water content. When the substrate was heat cured for 90 min in a drying furnace at 150°C, cylindrical photo via holes of 100 μm diameter were finely opened.

[0062]

After buffing the surface of the heat cured light sensitive composition by about 5  $\mu\text{m}$  to condition the surface, solvent swelling and chemical etching were conducted by an ordinary desmearing treatment and electroless plating was applied to form a copper foil to about 0.2  $\mu\text{m}$  thickness. Electric copper plating was applied thereon to obtain a copper plating layer of about 20  $\mu\text{m}$  in total. After forming a light sensitive etching resist (Photo ED system F-1000, manufactured by Nippon Paint Co.) on the copper plating, exposure was applied, using a copper circuit forming pattern mask, followed by development, etching and resist peeling to form a second layer conductor pattern on the light sensitive composition. After the step of laminating the light sensitive composition, the same steps were repeated to obtain a third layer conductor pattern. Subsequently, a solder resist was applied on the pattern to manufacture a multi-layered substrate having six layers in total. Conduction between each of the circuits was complete.

[0063]

In the step of copper plating after conditioning the surface of the light sensitive composition described above, a test plate with the copper plating thickness of 35  $\mu\text{m}$  in total was prepared and notched such that the width of the copper plating foil was 10 mm. When it was peeled at 90° by a tensile tester for measuring the adhesion strength between the copper

and lower comb patterns respectively and an insulation reliability test was conducted. The resistance value between the upper and lower layers was initially  $3 \times 10^{13} \Omega$  and the resistance value after 250 hr was  $6 \times 10^6 \Omega$ . This was an insulation reliability causing no problem at all in view of practical use.

[0064]

[Example 5]

A light sensitive composition with about 10% by weight of the organic solvent being left in the light sensitive composition was prepared while setting the drying time to about 50 sec when preparing the film-like light sensitive composition in Example 4. An insulative material made of glass epoxy previously formed with a conductor pattern was heated by being



passed through externally heating rolls set to 150°C. On the other hand, the film of the light sensitive composition described above and previously peeled with the polyethylene cover film was laminated on both surfaces of the insulative film by a vacuum laminator while being in contact with the rolls set to 40°C. After cooling the laminated substrate, a negative photomask was placed over the polyester base film for aperturing photo via holes, and it was exposed by an exposure machine using super high pressure mercury lamps at a light intensity of 600 mJ/cm<sup>2</sup> on the light sensitive composition. After peeling the polyester base film from the light sensitive composition, it was dried for 30 min in a drying furnace set at 80°C to remove the organic solvent. The not-exposed portion was dissolved with a 1% aqueous solution of sodium carbonate after washing with water, water content was removed by drying for 10 min in a drying furnace at 80°C. When the substrate was heat cured for 90 min in a drying furnace at 150°C, cylindrical photo via holes each of 100 µm diameter were opened finely. By the same subsequent steps as those in Example 4, a 6-layered substrate was obtained. The result for the peeling strength and the insulation reliability of the copper plating foil and the light sensitive composition of the obtained multi-layered substrate were identical with those in Example 4.

[0065]

[Effect of the Invention]

This invention can provide, at a high productivity, a multi-layered substrate having an insulation layer free from bubbles of deteriorating the insulation property, excellent in adhesion with the conductor pattern with no particular roughening treatment, capable of insuring electrical insulation property for a long period of time and excellent in the developability upon development.